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Modified cellulose fibers as adsorbent for dye removal from aqueous environment

Daniela Suteu[a,*], Sergiu Coseri[b], Carmen Zaharia[a,*], Gabriela Biliuta[b], Iulia Nebunu[a]

[a]*Gheorghe Asachi Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, 73 Prof. Ph.D. docent D. Mangeron Blvd, 700050 Iasi, Romania; emails: danasuteu67@yahoo.com (D. Suteu), czah@tuiasi.ro (C. Zaharia),*
[b]*Petru Poni Institute of Macromolecular Chemistry of Romanian Academy, Iasi, 41A, Gr. Ghica Voda Alley, 700487 Iasi, Romania; email: coseris@icmpp.ro (S. Coseri)*

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ABSTRACT

The paper proposes a new study of two cellulose-based materials tested as adsorbents for two models of dyes (i.e., anionic Brilliant Red HE-3B (BRed) and cationic Methylene Blue (MB) dye and characterized using advanced analysis techniques (Fourier-transform infrared /attenuated total internal reflection spectra, environmental scanning microscopy, X-ray diffraction analysis, viscosity measurements, average degrees of polymerization, and potentiometric titration) for providing the dye adsorption in the material structure. As main operational parameters in the dye adsorption: environment pH, adsorbent dose and initial dye concentration were investigated. The cationic MB dye, having a lower molecule size, is better retained on both tested adsorptive material types, that is, viscose fibers and oxidized cellulose (S114). Meanwhile, the oxidized cellulose sample was proved to be much efficient in the dye adsorption process than the viscose fibers, due to additional oxidative treatment supported which was introduced some high amounts of carboxyl groups, which was modified the behavior of both dyes in the adsorption systems. The description of BRed and MB dye adsorption onto S114 sample was performed by three adsorption models (Freundlich, Langmuir and Dubinin–Radushkevich) well being fitted the Langmuir (MB) and Freundlich (BRed) models, but also the maximum adsorption capacities (q_0) 25.25 and 454.54 mg/g, onto S114 adsorbent, for BRed and MB dye, respectively. The adsorption energy values (3.706–7.45 kJ/mol for BRed and 3.83–4.352 kJ/mol for MB dye) suggest that adsorption is probably a physical process that engages electrostatic interactions between the charged surface of the adsorbent and the corresponding ionic groups of the dyes.

Keywords: Adsorption; Brilliant Red HE-3B dye; Methylene Blue dye; Oxidized cellulose; Viscose fibers

1. Introduction

The organic dyes are chemical species with polluting potential that can be found in the surface waters discharged from different sources, such as, textile chemical finishing industry, paper, foods or chemical synthesis industry. Their removals are dictated by the produced effects like: affectation of aquatic life forms by visibility modification, degradation with liberation of chemical polluting compounds from the category of amines, etc. For removing such impurities from the aqueous environment, in-time numerous methods were developed: precipitation–coagulation, sonolysis, ionic exchange, adsorption [1–7], among others.

Till date, the adsorption remains a feasible alternative for treatment of wastewaters and surface waters, due to its efficiency, easiness in operating, possibility of selecting the most corresponding adsorbents for the analyzed system from a very vast range of adsorptive materials and with reduced costs.

Cellulose is a natural biodegradable polymer obtained from renewable resources. Cellulose-based materials can be found in many forms and types ranging such as fibers, linters, microcrystalline powders, softwood pulp, bacterial cellulose and many others.

The hydroxyl groups in anhydroglucose unit of cellulose are susceptible to be partially or fully converted with a

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* Corresponding author.

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wide range of reagents, to provide derivatives with beneficial properties. A way for chemical modification of hydroxyl groups from many others is the oxidation. The most used system for selective oxidation of the primary hydroxyl groups of cellulose, into carboxyl and/or carbonyl groups is 2,2,6,6-tetramethylpyperidine-1-oxyl radical (TEMPO) – NaBr – NaClO [8,9]. In this oxidizing system, TEMPO radical is activated by the hypobromide ions, which in turn are produced from sodium hypochlorite and bromide salt used as co-catalyst. The process is taking place at room temperature and pH range of 10–11. The TEMPO-mediated oxidation has been attracting a number of investigations since the first one reported by de Nooy et al. [10], which showed that only primary hydroxyl groups (OH–C6) of polysaccharides were oxidized, whereas the secondary hydroxyl groups (OH–C2, OH–C3) were remained unaffected.

The materials based on cellulose, due to its fibrous structure, high internal surface (determined by size and distribution of pores), increased hydroscopicity (correlated with the porous structure and presence of hydroxyl groups) and possibility of functionalization with organic reagents, have also developed numerous applications in obtaining materials with bioadsorptive properties [11–13].

In addition, cellulose and its oxidized derivatives possess several advantages as compared with synthetic polymers, such as biodegradability, biocompatibility and non-toxicity. Oxidized cellulose is of major interest for several biological applications with high impact on human life [12,14–18], such as hemostatic agent (oxidized cellulose is used in almost all kinds of surgeries) [19], bioabsorbable surgical thread [20], drug carrier [21], kidney dialyzer membranes [22], blood reducing agent [23], surgical lubricant [24], enzyme carrier [25] or bioadsorbable surgical network [26].

The availability to a low price, spherical form of particles, possibility of selecting the size of particles, mechanical resistance, great porosity, hydrophilia, compatibility with biological structures, ensuring of some rapid kinetics and functionalization susceptibility recommend these materials as candidates in range of efficient adsorbents both for polluting inorganic or organic species (colorants/dyes, phenols, pesticides, toxic metal ions, etc.) from wastewaters [13,27–35].

The main scope of this paper is represented by testing of the adsorptive potential of few fibrous materials based on oxidized cellulose in retaining of anionic and cationic organic colorants/dyes. In this context, it was evaluated the influence of some operating parameters (pH, colorant/dye type, cellulose-based type, initial colorant/dye concentration and adsorbent dose) onto removal of some organic anionic (Brilliant Red HE-3B [BRed]) and cationic (Methylene Blue [MB]) dyes from aqueous environment for identifying the optimal operational system of retaining and thoroughgoing of adsorption equilibrium study.

2. Materials and methods

2.1. Materials

2.1.1. Adsorbents

Viscose fibers (linear density (dtex) 1.88, average length: 39 mm, average diameter: 14.3 μm, degree of polymerization (DPv): 235, molecular mass: 38,500 g/mol, density: 1.5045 g/cm) were provided by Lenzing AG Austria. TEMPO (99% Sigma-Aldrich), sodium bromide (99% Alfa Aesar), sodium hypochlorite (NaClO, 3% chlorine, Chemical Company, Romania) were used without further purification.

2.1.2. Fiber preparation

Viscose fibers were washed with aqueous solution containing 200 mL of 0.1 M potassium chloride and 3 mL of 0.1 M hydrochloric acid. The resulting suspension was then stirred for 45 min in order to achieve complete wetting of the fibers and equal charge distribution.

2.1.3. Fibers oxidation

About 20 g viscose fibers were suspended in 400 mL deionized water, containing TEMPO (0.05 g) and sodium bromide (0.5 g). A certain amount of the 5 mmol/g cellulose in 3% NaClO solution was added slowly to the cellulose suspension to start TEMPO-mediated oxidation. The suspension pH was maintained to 10 at room temperature by adding a 2 M NaOH solution while stirring the suspension. The oxidation was then quenched after 2.5 h of stirring, by adding ca. 10 mL ethanol. The oxidized cellulose was thoroughly washed with distilled water and then freeze-dried and weighed to measure the mass recovery ratio.

Dyes: two selected dyes, that is, anionic BRed (Procion Red HE-3B; Reactive Red 120) with Colour Index (C.I.) 25,810, and cationic MB (Basic Blue 9) with C.I. 52,015 which are characterized in Table 1.

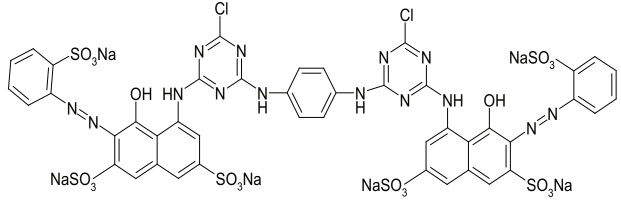
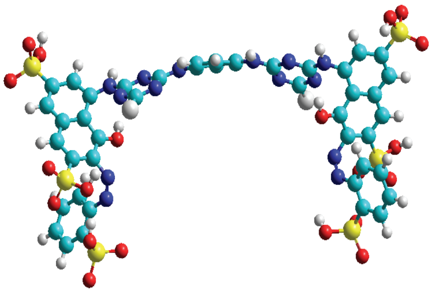
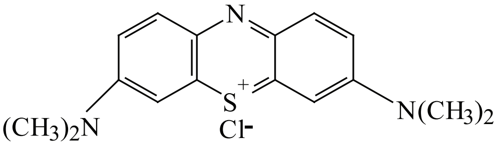
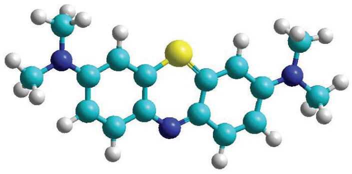
2.2. Methods

2.2.1. Methods for physicochemical characterization of cellulose adsorbents

2.2.1.1. Fourier-transformation infrared spectroscopy/attenuated total internal reflection spectroscopy The Fourier-transform infrared (FTIR)/attenuated total internal reflection (ATR) spectra of all samples were carried out on silicon single crystal parallelepiped internal refletion elements (55 mm × 5 mm × 2 mm, 45° incident angle), using a Bruker Vertex 70 instrument. All the spectra were the results of 256 coded scans at a resolution of 4 cm^{-1}. To give rise to C=O vibration band of the carboxylic groups, the treated cellulose adsorbents by selected oxidation were washed with diluted HCl (0.1 N) solution to convert the COO^-Na^+ groups into COOH ones.

2.2.1.2. Potentiometric titration The amount of negatively charged groups was determined using the potentiometric method. The pH potentiometric titration of the fiber suspension was carried out with a Mettler Toledo T70 titrator, in an inert atmosphere (N_2 bubbling), using a 10 mL burette. On average, 1 g of viscose fiber was suspended in a solution containing 0.1 M potassium chloride and 0.1 M hydrochloric acid and then stirred with a magnetic stirrer for about 30 min. The suspension was titrated in a forth and back manner between the initial pH of 2.5 to the preset pH of 11, using 0.1 M KOH solution. The pH value was measured using a Mettler Toledo DG-117 glass electrode. The same solution was also titrated

Table 1
Characteristics of the two studied dyes

Dyes	Characteristics
Brilliant Red HE-3B (BRed)  	An anionic bifunctional reactive dye, having molecular weight: MW = 1,463 g/mol and maximum absorption wavelength λ_{max} = 530 nm. It was used as aqueous solution with a concentration of the stock solution – 500 mg/L and prepared working solution with concentrations varying in the range of 25–400 mg/L
Methylene Blue (MB)  	A cationic phenothiazine dye, with MW = 319.85 g/mol and maximum wavelength λ_{max} = 660 nm. It is present in ionic form with chloride as the exchangeable ion. The aqueous dye stock solution of 320 mg/L was prepared by dissolving the corresponding amount of dye in double-distilled water. The working solutions were prepared by appropriate dilutions with concentration in range of 25.8–240.8 mg/L.

without the fiber sample as a blank acid–base titration for data evaluation purpose. The amount of negatively charged groups was calculated, by subtracting the blank titration from the sample titration. All presented values are the mean values from three parallel measurements, the standard deviation of all measurements being within 4%.

2.2.1.3. Environmental scanning microscopy Untreated and treated cellulose adsorbents were both investigated by a Quanta 200 Environmental Scanning, operating at 5 kV with secondary electrons in high vacuum mode. Fibers were fixed by means of colloidal silver on copper support. The viscose fibers were covered with a thin layer of gold, by sputtering (EMITECH 550×).

2.2.1.4. X-ray diffraction analysis X-ray measurements were made on pellets of viscose fibers (ca. 0.1 g was pressed). The sample was loaded onto the X-ray diffractor (D8 Advance Bruker) to analyze from 5° to 35° 2θ with data acquisition taken at 0.02° s^{-1} by the reflection method. The operated voltage was 30 kV and the current intensity was 36 mA.

2.2.1.5. Measurement of average viscosity and polymerization degrees Intrinsic viscosities of the cellulose fibers were obtained by a capillary viscometer using 0.5 M copper ethylenediamine (cuen) as the solvent. All these values were converted to viscosity average DPv according to the previous reported method [36].

2.2.2. Adsorption methodology

The experimental tests of adsorption were performed through the batch method, which supposed contacting different amounts of adsorbent with 25 mL of dye solution with different dye concentrations. The established values of initial solution pH were achieved by using aqueous 1 N NaOH and 0.1 N HCl solutions, which were measured with a HANNA pH/Ion analyzer. The constant temperature of adsorption process was maintained using a thermostatic bath. The adsorption systems have undergone to discontinuous stirring. After 24 h of contact phase, the residual dye concentrations in aqueous environment were determined using an UV–VIS digital spectrophotometer, model S 104D/WPA. Two most important quantitative characteristics were evaluated by means of amount of adsorbed dye and consequently adsorption capacities of the cellulosic materials [Eq. (1)]:

$$q = \frac{C_0 - C}{G} \times V \tag{1}$$

and the percent of dye removal [Eq. (2)]:

$$R,\% = \frac{(C_0 - C) \times 100}{C_0} \tag{2}$$

where C_0 and C are initial and the equilibrium concentrations of dye in solution (mg/L), G is the amount of adsorbent (g) and V is the volume of aqueous solution (L).

2.2.3. Analytical methods for quantitative determinations

The concentrations of dyes in aqueous samples were determined by spectrophotometer-based method using the absorbance at the maximum dye wavelength of 530 nm (BRed) and 660 nm (MB), respectively, with a UV–VIS digital spectrophotometer, model S 104D/WPA and interpolating using a calibration curve (the working concentration range was in the Lambert–Beer region).

3. Results and discussion

3.1. Characterization of cellulose adsorbents

3.1.1. Oxidized cellulose-based adsorbents

The reaction of oxidation was carried out by using stable nitroxyl radical, TEMPO, as mediator in the sodium hypochlorite – sodium bromide system. The real oxidizing species in this process is the nitrosonium ion, the oxidized form of TEMPO, which is generated in situ through the reaction of TEMPO with hypobromide ions, which in turn were generated from bromide salts and sodium hypochlorite. Furthermore, the nitrosonium ion is converted into *N*-hydroxy-2,2,6,6-tetramethylpiperidine, the reduced form of TEMPO [37].

The content of C6 oxidized groups has been determined by using potentiometric titration. The amount of carboxylate contents increases from 6 mmol/kg of cellulose in the cellulose adsorbents to 145 mmol/kg of cellulose in the case of oxidized cellulose-based adsorbent.

3.1.2. FTIR/ATR analyses

Fig. 1 shows comparative spectra of the unoxidized and treated cellulose-based adsorbents. It can be seen that the main features of the cellulose skeleton (3,100–3,500 cm^{-1} –OH stretching, H-bond, 2,900–2,950 cm^{-1} –CH stretching of –CH$_2$ and –CH groups, 1,650 cm^{-1} absorption band due to the adsorbed water, 1,050 cm^{-1} C–O–C stretching vibration) remain unaffected after oxidation, proving that the process does not destroy the intrinsic cellulosic structure. However, the major changes in the FTIR spectra after oxidation are observed in the 1,600–1,800 cm^{-1} range, due to the presence of a new adsorption band around 1,726 cm^{-1}, which corresponds to the C=O stretching frequency of carboxyl groups in the acidic form, this band is totally absent in the untreated cellulose adsorbents.

3.1.3. Morphological changes of cellulose adsorbents during TEMPO-mediated oxidation

Fig. 2 illustrates the ESEM microphotographs of the cellulose adsorbents and TEMPO-oxidized cellulose adsorbents. After oxidation, the cellulose adsorbents show insignificant regions of deterioration; only at the surface of cellulose fibers it seems to become rougher.

3.1.4. X-ray diffraction analysis

The comparison of diffraction diagrams of the cellulose adsorbents, before and after TEMPO-mediated oxidation, reveals that both shape and peaks of diffractograms are nearly identical. This is a clear indication that the crystallinity of the original sample is not affected by the oxidation treatment (the measured crystallinity was about 25% in both sample), the oxidation reaction in cellulose adsorbent occurs only at the fibril surface. This behavior suggests that the TEMPO-oxidation method could be a valuable technique for the activation of cellulose fibrils for the future applications, including adsorption of various dyes, due to its mildness and high selectivity on primary OH groups. Fig. 3 illustrates the X-ray diffraction patterns of cellulose adsorbents before and after oxidation, where can be observed the presence of two main peaks at 12.4° and 21° corresponding to the amorphous and crystalline regions.

3.2. Adsorption of reactive and cationic dyes on studied cellulose materials

For evaluation of adsorption capability in the case of these cellulose materials vis-à-vis of selected dyes as organic

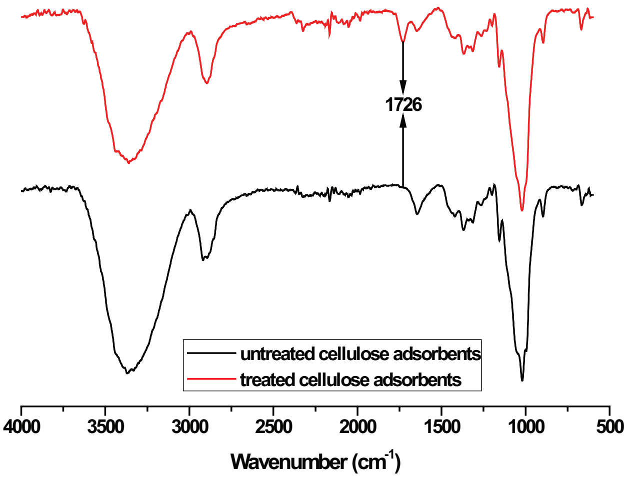


Fig. 1. FTIR spectra of the untreated and treated cellulose adsorbents.

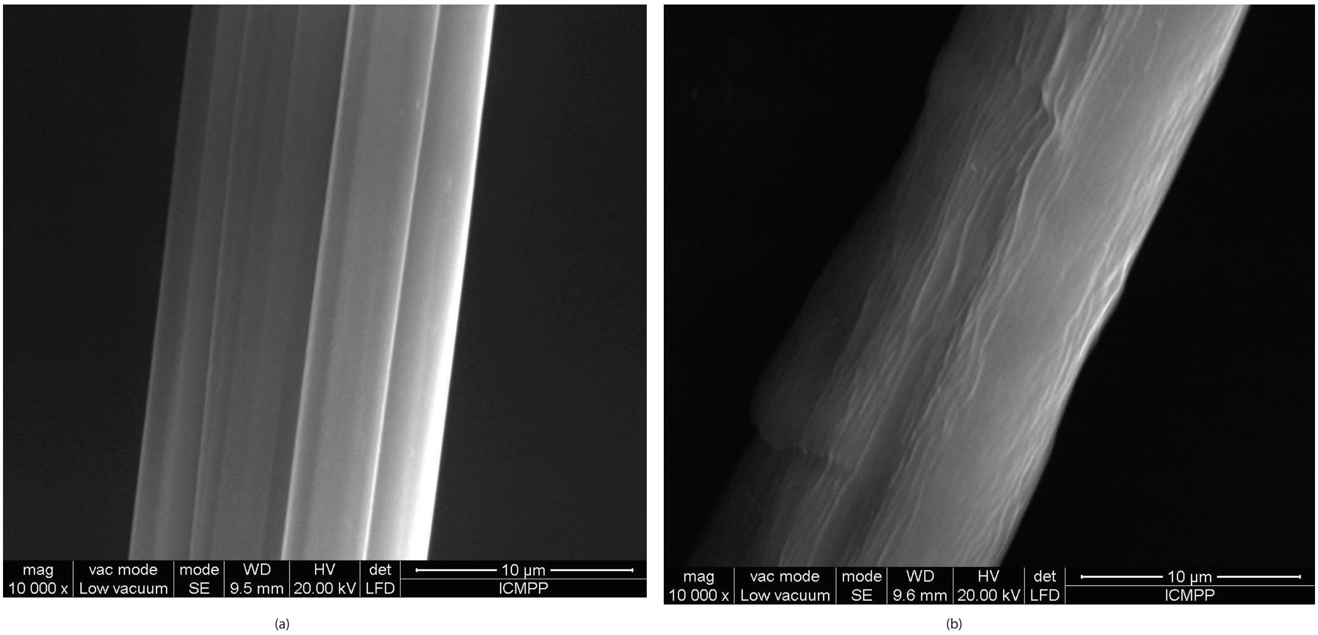


Fig. 2. ESEM microphotographs of the cellulose adsorbents before (a) and after (b) oxidation.

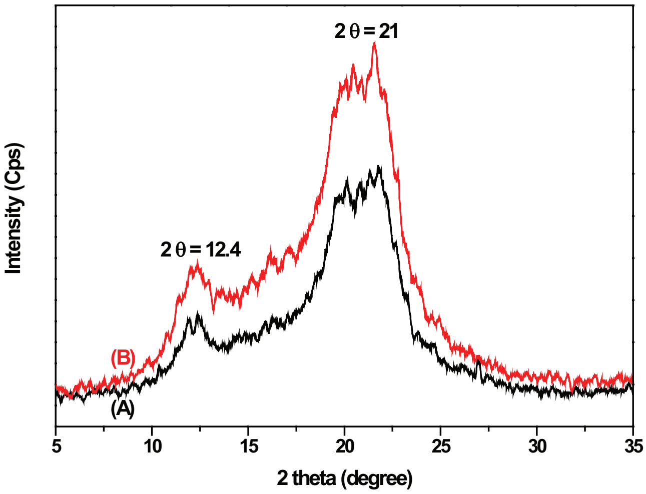


Fig. 3. X-ray diffraction patterns of cellulose adsorbents before (A) and after (B) oxidation.

pollutants of surface waters or residuals in treated wastewaters, experimental studies were performed for emphasizing the influence of a few physical–chemical operational parameters against the evolution/behavior of adsorption process.

3.2.1. Influence of solution pH

An extreme important operational parameter in the development of adsorption process is represented by the pH of colorant solution. This operational parameter determines both behavior of solid material used as adsorbent (modification of dissociation degree of functional groups from the structure of adsorbents, which determines a certain electric charging of their surface) and of organic species which must be retained from aqueous environment. In function of the pH value and also the charge of the adsorbent surface it would be possible to retain the anionic or cationic species from the aqueous environment.

The variation of dye uptake (q, mg/g) as a function of initial solution pH, presented in Fig. 4, suggested that the anionic dye could be better adsorbed from acidic media with pH 2, and cationic dye from basic environment with pH 11. This behavior may be a due to following reasons:

- the availability of dye exchange positions (i.e., $-SO_3H$ for BRed);
- the surface charge of the adsorbent which depends on the pH of the environment and can be explained as follows. These functional groups, COO^-Na^+, are dissociated at various pH values. At low pH (less than 4.0), carboxyl groups retain their protons (COOH) due to protonation, which weakens the interaction between negatively charged groups (COO−) and positively charged dye ions because a hydrogen ion in the solution can compete with a cation of dyes for active sites on the adsorbent surface. With an increase in pH of the solution, these functional groups became deprotonated (COO^-), which is resulted in an increase in the negative charge density on the adsorbent surface and is facilitated the binding of cation of dyes. Hence, the dye ions binding to the adsorbent mainly involved electrostatic interaction between cationic dyes and negatively charged COO^- groups, and the mechanism of the adsorption process is *physical adsorption* depending on electrostatic interaction.

3.2.2. Influence of adsorbent dose

To determine the optimal dose of cellulose-based adsorbents, diverse amounts of tested solid adsorptive materials were contacted with 25 mL of dye solutions with certain concentrations, at an established initial pH, for 24 h of contact time.

As seen in Fig. 5, an increase of the cellulose dose from 1.9 to 29.1 g/L induces an increase of the percentage of dye removal from 22.012% to 88.27%, but a decrease of the amount of reactive dye retained per unit weight of adsorbent from 6.976 to 1.82 mg/g. This behavior can be explained by the reduction of dispersion inside the solid adsorbent mass due to the dye steric effect and also the better retention of species only at the external surface of sorbent towards the inside solid structure.

3.2.3. *Influence of initial dye concentration and dye types*

The adsorption capacity of wet cellulose for the selected dye was determined in aqueous solutions with initial pH of 1.3 and various dye concentrations.

From Fig. 6, it is observed that the amount of retained dye increases with the increase of initial dye concentration which is contacted with the adsorbent. In addition, it is remarked that the retained dye amount depends on the colorant/dye type and also material structure and properties. Thus, the cationic MB colorant, with low size of molecules, it is better retained on both solid material types.

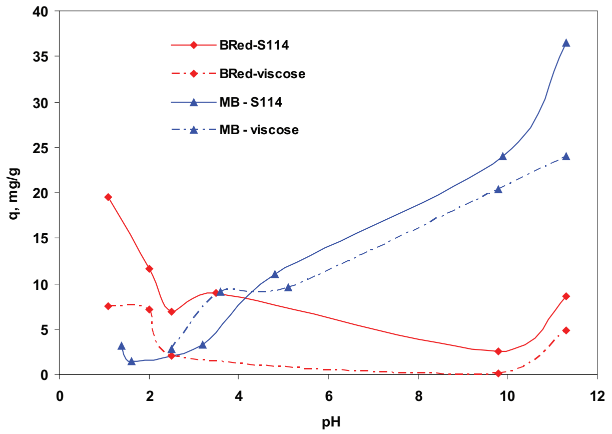


Fig. 4. The influence of environment pH on dyes (BRed and MB) adsorption at 20°C onto cellulose-based materials (0.8 g/L dose of S-114 and viscose). Conditions followed: $C_{0,\mathrm{BRed}}$ = 55.5 mg/ L, $C_{0,\mathrm{MB}}$ = 43 mg/L and 24 h of contact time.

3.3. *Modeling the adsorption equilibrium*

The adsorption isotherms are most comfortable tools for a first evaluation of adsorption equilibrium. These are obtained by the graphical representation of data in coordination, $q = f(C)$ (Figs. 7(a) and (b)). There are several different types of adsorption isotherms presented and characterized in the scientific literature [38,39]. These are mainly classified by the style of the shape, which is closely related to the type of solute and adsorbant, and the intermolecular interactions between the solute and the surface.

From Figs. 7(a) and (b), it is observed that the adsorption of tested colorants/dyes onto viscose fibers is of anti-Langmuir type, behavior registered at the systems where the solute–stationary phase interactions are weak related to the solute–solute interactions, the adsorbent being of mesoporous type.

An explanation could be the fact that the sample of oxidized cellulose-based adsorbent was experienced an additional treatment for introduction in the basic structure of cellulose of higher amounts of carboxyl groups, that modify the behavior in the sorption systems towards both organic dyes.

The modeling of experimental adsorption data can be made using three of the most used adsorption models: Freundlich, Langmuir and Dubinin–Radushkevich (DR) isotherms [38,39] [Eqs. (3–5)]. The obtained results are presented in Table 2.

The main Freundlich isotherm model assumption is that the surface is heterogeneous, and also the distribution of active sites of the adsorbent is exponential. The nonlinear/linear forms of equation are as follows:

$$q = K_F C^{1/n} / \log q = \log K_F + 1/n \log C \tag{3}$$

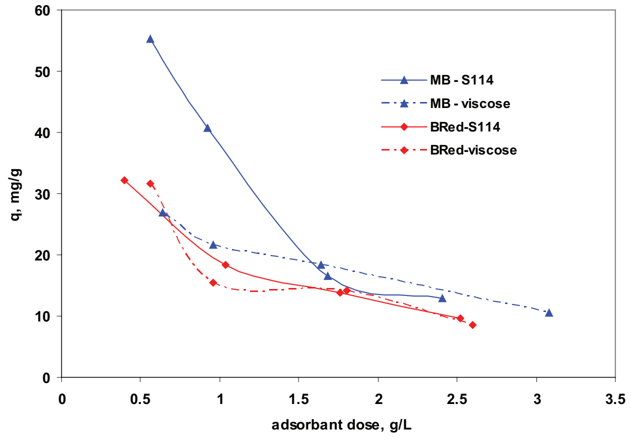


Fig. 5. The influence of adsorbent dose (S-114 and viscose) on dyes (BRed and MB) adsorption at 20°C onto cellulose materials. Conditions followed: $C_{0,\mathrm{BRed}}$ = 55.5 mg/L, $C_{0,\mathrm{MB}}$ = 43 mg/L; $\mathrm{pH}_{\mathrm{Bred}}$ = 1.1 or $\mathrm{pH}_{\mathrm{MB}}$ = 11.3 and 24 h contact time.

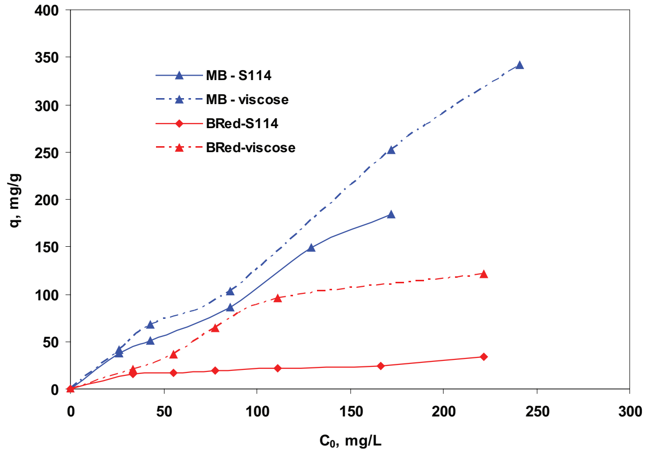
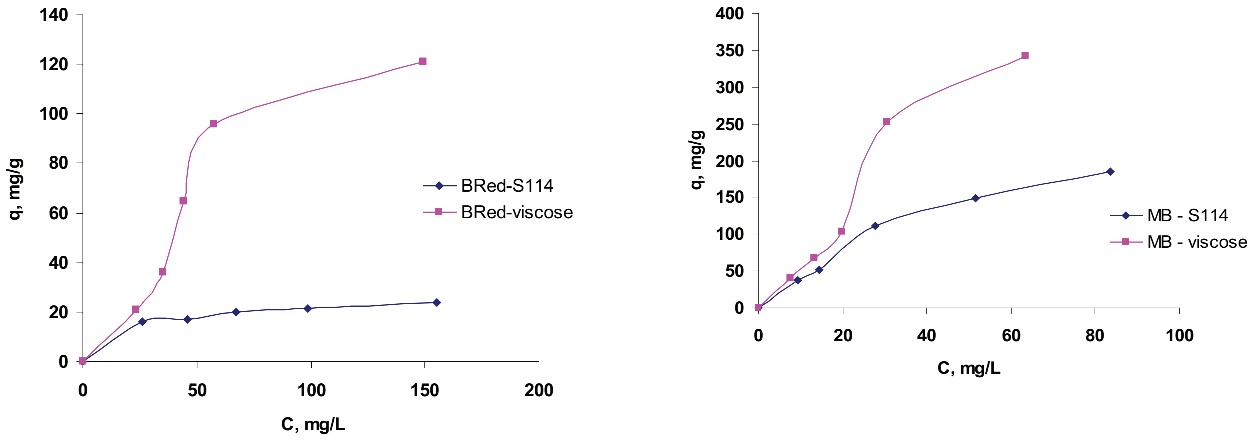


Fig. 6. The influence of initial dye concentration (BRed and MB) on adsorption at 20°C onto cellulose materials (S-114 and viscose). Conditions followed: $\mathrm{pH}_{\mathrm{Bred}}$ = 1.1 and $\mathrm{pH}_{\mathrm{MB}}$ = 11.3; 0.8 g/L adsorbent dose and 24 h contact time.



a

b

Fig. 7. Adsorption isotherms for retention of Brilliant Red HE-3B reactive dye (a) and Methylene Blue cationic dye (b) on different cellulose materials.

Table 2
Characteristic isotherm parameters for adsorption of BRed dye and MB dye onto cellulose materials

T, K	298			
Dye	BRed		MB	
Adsorbent	S114	viscose	S114	viscose
Freundlich isotherm				
K_F, (mg/g)(L/mg)$^{1/n}$	7.4012	1.429	7.313	4.569
n	4.305	1.07	1.366	0.929
R^2	0.9707	0.8135	0.9635	0.9536
Langmuir isotherm				
q_0, mg/g	25.25	–	454.54	–
K_L, L/mg	0.0588	–	0.00957	–
R^2	0.918	–	0.9848	–
Dubinin–Radushkevich (DR)				
q_0, mg/g	26.96	274.42	284.155	668.65
B, mol^2/kJ^2	0.009	0.0364	0.0264	0.034
E, kJ/mol	7.45	3.706	4.352	3.83
R^2	0.9559	0.898	0.982	0.9572

where K_F and $1/n$ are constants related to the adsorption capacity and adsorption intensity (efficiency), respectively; a favorable adsorption corresponds to a value of $1 < n < 10$.

The Langmuir isotherm model supposes that the maximum adsorption corresponds to a monolayer of solute molecules on the adsorbent surface, containing a finite number of energetically equivalent sites. The nonlinear/linear forms of this isotherm model are as follows:

$$q = \frac{K_L C q_0}{1 + K_L C} \Big/ \frac{C}{q} = \frac{1}{q_0 K_L} + \frac{C}{q_0} \tag{4}$$

where q_0 is the maximum amount of adsorbed solute (mg/g) and K_L is the constant related to the binding energy of solute (L/mg).

The DR isotherm model suggests the nature of the adsorption process – physical or chemical: $E < 8$ kJ/mol characterizes a physical adsorption mechanism and values between 8 and 16 kJ/mol indicates an ion exchange mechanism. The linear forms of equations are as follows:

$$q = q_D \exp(-B\varepsilon^2) / \ln q = \ln q_D - B\varepsilon^2 / \varepsilon = \mathrm{RT}\ln\left(1 + \frac{1}{C}\right) \Big/ E = \frac{1}{\sqrt{-2B}} \tag{5}$$

where q_D is the maximum sorption capacity (mg/g); B is the activity coefficient related to mean adsorption energy; ε is the Polanyi potential and E is the mean free energy of adsorption (kJ/mol).

The quantitative parameters associated to each adsorption isotherm model were evaluated from the intercepts and slopes of the corresponding linear plots (figures not shown). These, together with the correlation coefficients (R^2) which have been used to assess what model describes better the adsorption process of BRed and MB dyes onto cellulose materials, are presented in Table 2.

Analyzing the information from Table 2, it can conclude that the values of correlation coefficients (R^2) suggest that the adsorption of the two selected dyes onto cellulose-based adsorptive materials have different behaviors: Langmuir model characterizes the adsorption of cationic dye MB and Freundlich model describes very well the adsorption case of BRed dye. This validates the fact that there exists a strong dependence between implementation of the process and the studied adsorbent and dye structure.

The MB dye presents a lower size of molecules, fact that ensures a better diffusion in the material pores. In addition, in the operational conditions, all necessary elements for retaining of MB dye (basic medium) leads to an adsorbent chemistry much favorable to retain this colorant type to detriment of BRed dye. The maximum amount of dye retained in the mentioned conditions varies between 37.665 and 184.42 mg MB dye/g of S114 and 15.846–24.004 mg BRed/g of S114.

By using (DR) model, it can be indicated the physical or chemical nature of the adsorption process. The adsorption energy values obtained, in range of 3.706–7.45 kJ/mol for BRed dye and 3.83–4.352 kJ/mol in the case of MB, suggest that adsorption is probably a physical process that engages electrostatic interactions between the charged surface of the adsorbent and the corresponding ionic groups of the dyes. In addition, the type of adsorption could be influenced rather by physical forces than by chemical ones, depending on operational parameters of the process and also by the structure of dyes [40].

4. Conclusions

Oxidized cellulose (S114) and viscose fibers were synthesized using optimized experimental conditions obtained through a design planning of experiments and a response surface methodology. S114 and viscose fibers were characterized by FTIR/ATR spectra, ESEM, X-ray diffraction analysis, mean intrinsic viscosity, DPv measurement, and potentiometric titration in order to determine the amount of negatively charged groups.

The S114 and viscose were effective as adsorbents in the removal of the selected model dyes, BRed and MB, from aqueous environments. All experimental results indicate that the dye retention depends on several physical–chemical operational parameters (solution pH, contact time, adsorbent dose, dye concentrations, type of dye and adsorbent) and is more effective for system S114 – MB, fact explained by the structures of both adsorbent and dyes. The adsorption isotherms were evaluated by three adsorption models and the experimental data fitted well to the Langmuir (MB) and Freundlich (BRed) models. Maximum adsorption capacities (q_0) for BRed and MB on S114 were found to be 25.25 and 454.54 mg/g, respectively. The adsorption energy values obtained using DR isotherm model, in range of 3.706–7.45 kJ/mol for BRed dye and 3.83–4.352 kJ/mol in the case of MB dye, suggest that adsorption is probably a physical process that engages electrostatic interactions between the charged surface of the adsorbent and the corresponding ionic groups of the dyes.

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